Japanese Published Unexamined (Kokai Koho) Patent Application (A) No. 05-262981, published October 12, 1993; Application No. 04-91562, filed March 18, 1992; Int.Cl.: C 08 L 79/00, C 08 K 3/24, 5/42, C 08 L 25/18, H 01 B 1/12; Inventor(s): Toshiroo Watanuki et al.; Assignee: Nippon Kaaritto Corporation; Japanese Title: Water-Dispersible Polyaniline Component and Manufacturing Method Therefor

---

WATER-DISPERSIBLE POLYANILINE COMPONENT AND MANUFACTURING METHOD THEREFOR

CLAIM(S)

1) A water dispersible polyaniline component characterized by its being composed of polyaniline containing low molecular proton acid as a dopant and of polystyrene sulfonate with mol weight 50,000 or higher as a water dispersing agent.

2) A water dispersible polyaniline component, as mentioned in Claim 1, wherein an oxidant is added for polymerization by oxidation while keeping pH in the range of 2 - 5.

3) A water dispersible polyaniline component, as mentioned in Claim 1, wherein the polystyrene sulfonate is ammonium salt, alkyl ammonium sat or alkaline metal salt.

4) A water dispersible polyaniline component, as mentioned in Claim 2, wherein polystyrene sulfonate is ammonium salt, alkylammonium salt or alkaline metal salt.

DETAILED DESCRIPTION OF THE INVENTION

(0001)

(Industrial application)

The present invention pertains to water-dispersible polyaniline component and manufacturing method therefor.

(0002)

(Prior Art)

Recently, extensive studies are being conducted regarding the application of conductive macromolecules, e.g., polyacetylene, polypyrrole, polythiophene, and aniline, for a new conductive material, solid electrolyte for condensers, electrode for batteries, anti-static material, various sensors, and as display devices. These macromolecules, however, are generally insoluble in solvent, therefore, are difficult to mold or process for their being insolubility.

(0003)

There is a report on solvent-soluble polyaniline that is improved in solubility. For example, aniline is chemically polymerized by oxidation in the presence of organic sulfonate such as polystyrene sulfonate to produce soluble polyaniline ("Synthetic Metals" by Suzhen Li et., Vol. 20, 1987, p. 141). Also, Japanese Unexamined Patent Application 01-254764 discloses water-soluble conductive

organic polymer and its manufacturing method, wherein aniline is chemically polymerized by oxidation in the presence of water-soluble organic macromolecular protonic acid, such as polystyrene sulfonate with an oxygen dissociation constant 3.0 or less. Both of the above use protonic acid, such as polystyrene sulfonate, as a dopant, and polyaniline is dissolved by sulfonic acid that does not interfere with the dopant.

(0004)

When polystyrene sulfonate is used as a dopant, moldability and processability are improved, but the conductivity is poor, and by dissociated sulfonic acid radicals that does not interfere with doping, the solution becomes strongly acidic (pH 2 or less in 1 wt% solution). If it is used for an antistatic material, there will be a problem that a contacted metal will be corroded.

(0005)

Moreover, in Japanese Unexamined Patent Application 02-240139, a method to manufacture a polyaniline-dispersed solution, whereby aniline compound is polymerized by oxidation in the presence of nonionic macromolecules, ampholytic macromolecules, and of a surfactant, and a conductive macromolecular material made of polyaniline-dispersed solution are disclosed. The inventors, however, found after testing it that, in the manufactured polyaniline-dispersed solution, the particle

diameter was large, and the dispersion was unstable. Moreover, they found that if the polyaniline compound is dissociated from the polyaniline-dispersed solution by repeated sedimentation, it would be difficult to make the water-dispersible solution again.

(0006)

(Problems of the Prior Art to Be Addressed)

The objective of the present invention aims to present a water-dispersible polyaniline component which is free from these problems. More specifically, the dispersing property of a polyaniline component is improved in its moldability and processability, and the pH of the dispersion solution is made more neutral to avoid the corrosion of metal; thereby the present invention presents a water-dispersible polyaniline component and manufacturing method therefor.

(0007)

(Means to Solve the Problem)

The inventors, after having studied from various standpoints, found a water-dispersible polyaniline component and it manufacturing method, and produced the present invention.

(0008)

The present invention present a water dispersible polyaniline component

characterized by its being composed of polyaniline containing low molecular protonic acid as a dopant and of polystyrene sulfonate having mole weight 50,000 or more as a water dispersing agent, and the method therefor, wherein an oxidant is added to the solution containing aniline and polystyrene sulfonate with mol weight 50,000 or more, while keepting the pH in the range or 2 -5, to conduct polymerization by oxidation.

(0009)

The present invention is explained in detail below. As to the low molecular protonic acid used as a dopant in the present invention, for example, the following can be cited: hydrochloric acid; sulfuric acid; perchloric acid; mineral acid such as tetrafluoroborate or hexafluorophosphate; single molcular organic sulfonate such as benzenesulfonate or p-toluenesulfate. They are supplied as acid generated by decomposition of acid or of an oxidant contained in aniline.

(0010)

The polystyrene sulfonate used in the present invention has mol weight 50,000 or more. With the mol weight 50,000 or less, polyaniline cannot be easily dispersed in water. As to the polystyrene sulfonate, ammonium salt, alkyl ammonium salt or alkaline metal salt can be cited. For example, they are: polystyrene ammonium sulfonate; monomethyl ammonium polystyrene sulfonate; dimethyl ammonium

polystyrene sulfonate; trimethyl ammonium polystyrene sulfonate; tetramethyl ammonium polystyrene sulfonate; ethyl ammonium polystyrene sulfonate; diethyl ammonium polystyrene sulfonate; triethyl ammonium polystyrene sulfonate; tetraethyl ammonium polystyrene sulfonate; propyl ammonium polystyrene sulfonate; dipropyl ammonium polystyrene sulfonate; tripropyl ammonium polystyrene sulfonate; butyl ammonium polystyrene sulfonate; ammonium salt or alkyl ammonium salt of polystyrene sulfonate such as pentyl anmmonium polystyrene sulfonate or hexyl ammonium polystyrene sulfonate; alkali metal salt of polystyrene sulfonate such as sodium polystyrene sulfonate, potassium polystyrene sulfonate, or lithium polystyrene sulfonate. But the polyethylene sulfonate is not limited to the above.

(0011)

As to the amount of polystyrene sulfonate to be used, it varies depending on the mol weight but, provided that A (mol/mol) = (polystyrene sulfonate monomer unit)/(aniline), A is 0.5 - 10, more preferably, 1-5. If A is 0.5 or less, the water dispersible polyaniline component cannot be easily produced, and if A is more than 10, the conductivity is dropped.

(0012)

Said water-dispersible polyaniline component of the present invention is

composed of polyaniline containing said low molecular protonic acid as a dopant and of said polystyrene sulfonate, and can be produced by polymerization by oxidation, in which an oxidant is added to a solution containing aniline and polystyrene sulfonate with mol weight 50,000 while keeping pH in the range of 2-5.

(0013)

As to the aniline salt used in the present invention, the following can be cited: hydrochlorate of aniline; sulfate; perchlorate; mineral acid of tetrafluoroborate or hexafluoroborate; single molecular organic sulfonate such as benzene sulfonate or p-toluene sulfonate. They may use the salt of aniline or can be synthesized in an reaction chamber by adding equivalent amount of mineral acid or single molecular organic sulfonate to aniline.

(0014)

In the present invention, the initial pH of solution of aniline salt and of polystyrene sulfonate is 2 - 5. The polymerization by oxidation is conducted by adding an oxidant while keeping the initial pH. To keep the initial pH during the reaction, base is added if needed. As to the base, there can be cited: sodium hydroxide; alkali such as potassium hydroxide or lithium hydroxide; amine such as ammonia, methyl amine, ethyl amine or triethyl amine.

(0015)

As to the oxidant used in the present invention, there can be cited: ferrous chloride; boron trifluoride; metal halide such as arsenic pentafluoride or alumminum chloride; peroxide such as perhydroxide or benzoylperoxide; persulfate or its salt such as persulfate, ammonium persulfate or potassium persulfate; perhalogen acid or its salt such as periodic acid, potassium perchlorate, or ammonium perchlorate; transition metal compounds such as potassium permanganate and ammonium dichromate; oxygen; ozon. Each of them can be used by itself or two or more can be combined for use. The amount of the oxidant used varies depending upon its type; it generally 0.1-10 mol, more preferably, 0.3-5 mol to 1 mol of aniline salt.

(0016)

The reaction temperature of the polymerization by oxidation is not specifically limited, but the range of -5°C - a normal temperature is preferred to enhance the conductivity of water dispersible polyaniline component. The reaction time is 0.2-100 hours, more preferably, 1- 10 hours.

(0017)

In the present invention, water is generally used as a solvent, so the reaction solution is dispersed in water. The separation or refinining of the water-dispersible

polyaniline component is done by the following method: 1) water dispersed solution is put in the hydrophilic organic solvent, and sedimented for filtering, or the produced sediment is dispersed in water, and the same operation is repeated; 2) water dispersed solution is put to dialysis; 3) water dispersed solution is filtered.

(0018)

The water-dispersible polyaniline component of the present invention can be mixed, for example, with an emulsion or solution of a general urethane resin, melamine resin, vinyl chloride resin, acrylic resin or polystyrene resin, and by coating the admixture on the insulating substrate, the surface can be provided with conductivity, and the transparency can be retained by controlling the thickness of the coating film.

(0019)

(Embodiment Example)

The present invention is explained further with reference to the embodiment example. In each embodiment example, the mol number of polystyrene sulfonate is expressed by monomer unit. The conductivity was measured by applying 2200 Kg/cm^2 pressure by use of a hydraulic molding machine to form pellets (diameter 13 mm x thickness 1-2) from the water-dispersible polyaniline component and by bonding a conducting wire with a silver paste by a two-terminal method in the air.

In addition, the particle diameter of the component was measured by a submicron particle analyzer N4 type made by Nikka Kisei Koruta.

(0020)

(Embodiment Example 1)

To a solution prepared by mixing sulfuric acid 0.49 g (m mol) and water 25.9 g, aniline 0.93 g (10 m mol) was added, and an ammonium polystyrene sulfate (mol weight 120,000) 30 weight% solution was added by 20.1 g (30 m mol). The pH of the solution was 4.0. After the solution was cooled to 0°C, a solution, in which ammonium persulfate 1.14 g (5 m mol) was dissolved in water 10g, was dripped for 30 minutes, and agitated for two hours. During the reaction, high ammonia concentration water was dripped, and the pH was kept in the range of 2 - 5. After the reaction, the solution was put into acetonitrile 300 ml, and subsequently the sediment was cleaned with isopropyl alcohol, filtered, and dried; thus the water dispersible polyaniline component 5.8 g was produced.

(0021)

The conductivity of the component was 6×10^{-3} S/cm, and the average particle diameter was 70 nm. The pH of the water-dispersible solution having the component 1 wt% was 3.1. When it was filtered through a filtering paper No. 5B (approximately 4 μm pore diameter) and through a membrane filter with a 0.45 μm

pore diameter, there was no residue found on the filers. When the water dispersible solution was made alkaline by an ammonia solution, undoped, and analyzed by ion chromatography (Ion Chromatography Analyzer IC-200 made by Yokogawa Electric Corporation), a HSO_4^- content as a dopant was detected.

(0022)

The water dispersible solution was stable without the sedimentation of particles after left at a normal temperature for 6 months.

(0023)

A water soluble polyurethane resin 3 g (ORESTA UD -100N made by Mitsui Toatsu Chemical Corporation, concentration 30%) was added to the water dispersible solution 97g, and was coated on a polyethylene terephtharate film by #12 bar coater, heated at 120°C, dried, to produce a green clear coated film. The surface resistance of the coated film was 1 x 10 Ω/␣.

(0024)

(Embodiment Example 2)

Aniline 0.93 g (10 m mol) was added to the solution mixed with sulfuric acid 0.49 g (5m mol) and water 12.2 g, and the lithium polystyrene sulfonate (mol weight 70,000) 17 wt% solution was added by 33.5 g (30 m mol), and was cooled to 0°C. The pH of the solution was 4.9. A solution prepared by dissolving the ammonium

persulfate 1.14 g (5 m mol) in water 10 g was dripped at 0°C for 30 minutes, and was agitated for 2.5 hours. During the reaction, lithium hydroxide 10 wt / solution was dripped and its pH was kept in the range of 2-5. After the reaction, it was put into acetonitrile 150 ml, and was decanted. To this solution, isopropyl alcohol 100 ml was added, the sediment was filtered, dried, and the water-dispersible polyaniline component 5.5 g was produced.

(0025)

The conductivity of the component was 5 x 10^{-3} S/cm, and the average particle diameter was 80 nm. The pH of the component 1 wt% water-dispersible solution was 3.2. When it was left at a normal temperature for 6 months, it was stable without the sedimentation of particles.

(0026)

(Embodiment Example 3)

The water-dispersible polyaniline component 7.0 g was produced by the same method as that in Embodiment Example 1 except that ammonium persulfate 2.28 g (10 m mol) was used. The conductivity of the component was 5 x 10^{-3} S/cm and its water dispersibility was excellent.

(0027)

(Embodiment Example 4)

The water dispersible polyaniline component 2.9 g was produced by the same method as in Embodiment Example 1 except that an ammonium polystyrene sulfonate (mol weight 120,000) 30 wt% solution (10 m mol) was used by 6.7 g (10 m mol). The conductivity of the component was 8 x 10^{-2} S/cm, and its water dispersibility was excellent.

(0028)

(Embodiment Example 5)

Triethylamine 3.03 g (30 m mol) was added to 27.6 g of polystyrene sulfonate 20 wt% solution having mol weight 70,000, and the triethyl ammonium polystyrene sulfonate solution was prepared. On the other hand, a solution was prepared by adding aniline 0.93 g (10 m mol) to the mixed solution of sulfuric acid 0.49 g (5 m mol) and water 111 g. To this prepared solution, the triethyl ammonium polystyrene sulfonate solution prepared earlier was added and was cooled at 0°C. The pH of the solution was 4.5. The solution, in which ammonium persulfate 1.14 g (5m mol) was dissolved in water 10 g, was dripped for 30 minutes and was agitated for 30 minutes. During the reaction, triethylamine was dripped, and the pH was kept in the range of 2-5. After the reaction, the reacted product was put into

acetonitrile 300 ml, and its sediment was filtered and dried; thus, the water dispersible polyaniline component 1.8 g was produced. The conductivity of the component was 1 x 10^{-2} S/cm, and the average particle diameter was 60 nm. The component 1 wt% water dispersible solution had pH 3.1 and excellent water dispersibility.

(0029)

(Comparison Example 1)

Aniline 0.485 g (5.22 m mol) was added to the solution prepared by mixing 27.6 g of the polystyrene sulfonate (mol weight 70,000) 20 wt% solution and water 159 g. The pH of the solution was 1.1. After the solution was cooled to 5°C, the solution prepared by dissolving ammonium dichromate 0.429 g (1.7 m mol) in water 26 g was dripped for 30 minutes and agitated for 1 hour. The pH after the reaction was 1.2. After the solution, the reacted product was put in acetonitrile 550 g, and the sediment was filtered, washed with acetonitrile and isopropyl alcohol, and dried; thus, the polyaniline component 5.4 g was produced.

(0030)

The conductivity of the component was 1 x 10^{-3} S/cm. When the component 1wt% water dispersible solution was filtered by No. 5B filter, the membrane filter with pore 0.45 diameter was clogged. The water dispersible solution had pH 1.6 and

32 times higher acid concentration than that of Embodiment Example 1.

(0031)

When the water dispersible solution was made alkaline with ammonia and analyzed by ion chromatography, inorganic anion was not detected. In this example, only polystyrene sulfonate was used since there was no supply of low molecular protonic acid (the oxidant decomposing component does not contain anionic seed).

(0032)

(Comparison Example 2)

In Embodiment Example 1, the polyaniline component was produced by the same method as in Embodiment Example 1 except that ammonium polystyrene sulfate with mol weight 10,000 was used in stead of ammonium polystyrene sulfonate with mol weight 120,000. The component 1 wt% water-dispersible solution had poor water dispersibility and did not pass through the filter.

(Comparison Example 3)

After water 100 ml was added to aniline 10 g (0.108 mol), dense hydrochloric acid 15 g (0.148 mol), polyvinyl alcohol (DenKa PoBaru B-17 made by Electrochemical Corporation, saponification degrees 87-89) 5g, and sodium dodecyl benzene sulfonate 0.01 g, a solution prepared by dissolving ferrous chloride and

hexahydride (0.107 mol) in water 30 ml was dripped at a normal temperature for 30 minutes and was agitated for 2 hours. When this product was filtered by No. 5B filter paper, the filter paper was clogged. After 30 minutes, the polyaniline component sedimented on the filter paper was put into acetone 450 ml and decanted. Then, it was washed twice with acetone 200 ml, filtered, and vacuum-dried. When water 99 g was added to the produced component 1 g and agitated for 1 day, it was not dispersed in water at all.

(0034)

In the present invention, a water-dispersible polyaniline component can be produced by a simple method, wherein an oxidant is added to a solution containing aniline salt and polystyrene sulfonate with mol weight 50,000 or higher while keeping the pH in the range of 2-5 or polymerization by oxidation. The polyaniline component of the present invention has a small diameter; its water dispersibility is stable over time; it is excellent in moldability and processability. Its insulating substrate can be provided with conductivity by a simple method of coating or immersion. The pH of the water-dispersible solution is more neutral than when polystyrene sulfonate is used as a dopant, so the metal corrosion will not happen.